Laser Flash Diffusivity Measurement

of Diamond Films: "Some Experimental Specificities" 1

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ABSTRACT

A Laser Flash technique with fast infrared detection for the measurement of the normal diffusivity of thin films is presented in this paper. The experimental apparatus deviced for such a measurement is described. Some points specific to the difffusivity measurement of thin films of semi-transparent and highly conductive materials such as diamond, are discussed. Particularly, difficulties in connection with the good conductivity and weak thickness of the films we consider are pointed out. Finally, experimental results performed within the framework of the Diamond Round Robin 2 tests for both non-diamond and diamond films are presented and the influence of the coupled conductive-radiative heat transfer is shown.

KEY WORDS: coupled conduction and radiation; diamond films; heat transfer; laser flash stimulation; normal diffusivity; semi-transparent films; transient technique.

1. INTRODUCTION

Current industrial needs concerning thin films are becoming more and more important in many domains such as mechanics (friction), electronics (heat dissipation) or optoelectronics (light conduction) and require the developpement of new materials and the design of new coatings. Chemical-Vapor-Deposited (C.V.D) polychristalline diamond films are an example of such a developpement. Measurement of their thermophysical properties is very tricky, because of their not completely known composition ans structure and of their small thickness and good conductivity [1]. Their anisotropic properties [2] require the measurement of both in-plane [3,4,5] and perpendicular to the plane diffusivities. The *Laser Flash Method* is a commonly used method for the measurement of the normal diffusivity of bulk products. It can be extended for the measurement of thin films.

2. PRINCIPLE OF THE MEASUREMENT

The *Flash Method* consists in a heat pulse stimulation φ_0 (J.m⁻²) of the front face of the sample. The variation of the rear-face temperature with respect to time t is then considered. The normalized rear face thermogram with respect to its maximum is a function of both diffusivity and heat losses (see Fig. 1.). Let K be the thermal conductivity of the sample, e being its thickness. The transient thermal response of the rear face is given by the solution of the one-dimensional heat flow equation:

$$\frac{\partial^2 T(x,t)}{\partial x^2} = \frac{1}{D} \frac{\partial T(x,t)}{\partial t} \tag{1}$$

with the following bounderies conditions:

$$\bullet \quad T(x,0) = T_a \tag{2}$$

$$\bullet \quad -K \frac{\partial T(x,t)}{\partial x} \bigg|_{x=0} = \varphi_0 \delta(t) - h_1 (T(0,t) - T_{\infty})$$
 (3)

•
$$-K \frac{\partial T(x,t)}{\partial x}\Big|_{x=e} = h_2 (T(e,t) - T_{\infty})$$
 (4)

D being the thermal diffusivity of the sample and T_a the ambiant temperature.

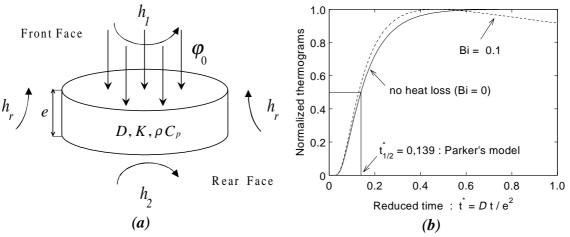


Fig. 1. Theoretical model

For a thin and good conductivity film, the Biot number Bi = he/K is low and heat losses can be neglected. In this case, the expression of the rear-face normalized temperature T^* is given by the expression:

$$T^*(e,t) = \frac{T(e,t) - T_a}{\rho C_p e} = 1 + 2\sum_{i=1}^{\infty} (-1)^i \exp\left(-(i\pi)^2 \cdot \frac{Dt}{e^2}\right)$$
 (5)

Parker and al.[6] showed that the half rise time $t_{1/2}$ is a function of the diffusivity:

$$t_{1/2}^* = \frac{D t_{1/2}}{e^2} = 0.139 \rightarrow D = 0.139 \frac{e^2}{t_{1/2}}$$
 (6)

An alternate method has also been used with estimation of the diffusivity by a Gauss-Newton's Non Linear Least Squares Method [7] based on the model given by Eq. (5) written in the Laplace domain and followed by a numerical Laplace inversion.

3. EXPERIMENTAL APPARATUS

Due to the very short response time and high diffusivity of the materials we consider, an experimental bench with a large bandwidth has been assembled. Thus, optical devices have been used for both stimulation (pulsed laser beam) and measurement (cooled infrared detector). A schematic representation of the experimental apparatus is given in Fig. 2.

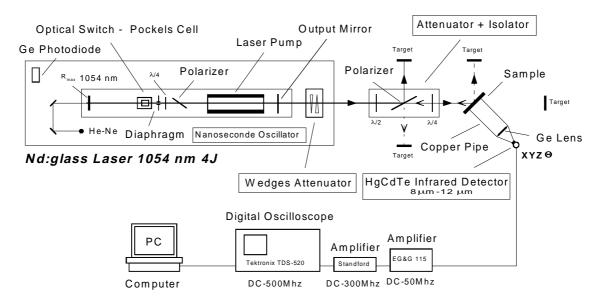


Fig. 2. Schematic scheme of experimental apparatus

• Laser Flash Stimulation

The stimulation is produced by a Nd:Glass laser (1054 nm) which delivers a pulse by an optical switch (Pockels's cell) with a duration less than 20ns. The diameter of the flat beam is 13 mm.

The 4J maxium intensity of the beam can be reduced continuously by the use of two attenuators. A two-wedges attenuator first reduces the energy by absorption. The output beam then passes through an optical isolator assembly which prevents high power back reflection into the cavity. This is composed of three elements: Half wave plate - Dielectric beamsplitter - Quarter wave plate. The rotation of the beamsplitter allows a continuous reduction of energy. So, one can make measurements with different kind of samples that require different levels of incident energy (conductive, dielectric, reflective or absorbing samples, with different thicknesses).

• Temperature Measurement

Measurement of the rear-face temperature is made by a high cutoff frequency cooled infrared photovoltaïc HgCdTe detector (>500 Mhz) (transmission window [8µm-12µm]). Its detectivity is high (D^* =8,7 10^{10} cm.Hz^{-1/2}W⁻¹). The signal is then amplified by a fast preamplifier and with a large bandwidth (DC-50Mhz), matched to the fast response time of the samples and with a large input impedance (1M Ω). This can be coupled with another amplifier to increase the amplification factor. The analogical signal is then digitized by a high frequency digital oscilloscope (500 Mhz) before to be treated by a computer. If the sample is far from the detector, a converging germanium lens (reflective to the laser beam wavelength) can be placed between the sample and the detector to focus the rear face emitting flux towards the sensitive element. In order to limit the influence of the outside radiative environment, a reflective cavity (copper pipe) can be inserted between sample and detector. It is especially interresting for our application which requires a coupled DC measurement to reduce the continuous signal component and to amplify only the interresting one's (amplifier overloading).

Because of the low emissivity of the copper pipe, the ambiant intensity is suppressed and the signal is only composed of the forward intensity coming from the sample. The cooper pipe also allows an increase of the apparent configuration factor between the sample and the detector.

• Difficulties caused by a non-uniform excitation

The 1D model that has been used for the measurement of the diffusivity requires that heat transfer within the medium is unidirectional. A theoretical and experimental study has been made to evaluate the 2D effects on the rear face temperature caused by the space reduced stimulation and the non uniform laser beam (Gaussian and flat laser profiles have been considered). This study shows that if the whole face is stimulated by a non uniform beam, then the local temperature mesurement (with a germanium lens) is strongly affected by two dimensioneal effects caused by in-plane heat diffusion at the end of recording. Thicker the samples are, stronger these effects are pronounced. These may be partially corrected with the use of the reflected cavity pipe instead.

• Coatings for semi-transparent samples

For the measurement of the normal diffusivity of semi-transparent films, a coating must be deposited on the film in order to make its faces opaque. This also allows a surface absorption of the energy of the heat pulse by the sample "front-face" and emission of the "rear-face" in order to allows a surface temperature measurement by a contactless radiation detector. The effect of the coating is especially important for thin films. To limit the coating thermal resistance, one usually uses thin metallic coatings that are generally poor infrared absorbers and emitters. Consequently, the level of the signal (temperature) measured by the infrared detector is low.

The coatings which appears to be a compromise solution are Gold/Palladium, Titanium, Gold/Titanium/Platinium. One also uses a "black powder" made of monoxyde of chromium and monoxyde of silicium for thicker samples. This presents high absorption and emission coefficients. Its semi-transparence requires the simultaneous use of a titanium coating for semi-transparent materials. Deposition of this powder on the two faces of an originally non-coated duraluminium sample produces a ten times increase of the measured signal.

4. EXPERIMENTAL RESULTS

In this section, results performed within the framework of the diamond Round robin II are presented. Titanium's coatings have been used for both non-diamonds and diamonds films.

• Non-Diamond films

The Fig. 3. illustrates the thermograms obtained for Titanium coated non-diamond films with two different thicknesses ($630\mu m$ and $250 \mu m$).

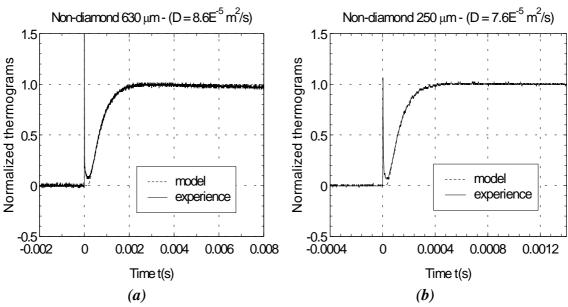


Fig. 3. Non-diamond films of different thicknesses

This shows the effect of the thickness on the Signal/Noise ratio (thinner the film, larger the ratio). One can observe the semi-transparence effect of the sample by a *temperature jump* at the very early times on the rear face thermogram. One can also notice a 2D effect for the thicker sample (heat losses cannot appear at this time). The semi-transparent effects are not systematic: thermograms for two different ceramics (low and high absorption coefficients) of roughly the same thickness are presented in Fig. 4.a. and b. No *peak* is apparent on the second figure for the more absorbing medium.

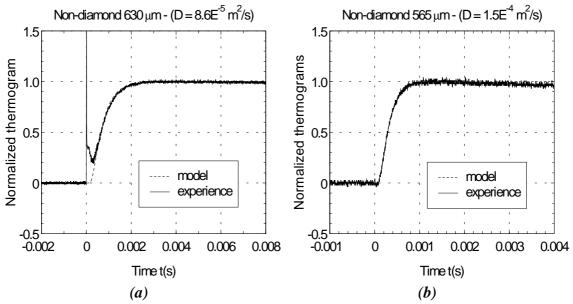


Fig. 4. Non-diamond films with different absorption coefficients

The appearance of a *peak* can be explained by two phenomena: first, a direct radiative transfer between front and rear face and second, defects in the coatings. If the front face is partially transparent, the rear face is directly insolated by the laser beam. Thus, the signal measured is a combination of both front and rear faces responses. The effects are very important for thin and transparent samples (effect of the *optical thickness*).

• Diamond films

Fig. 5. shows a perfect response for a diamond film.

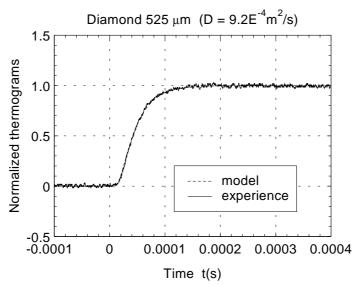
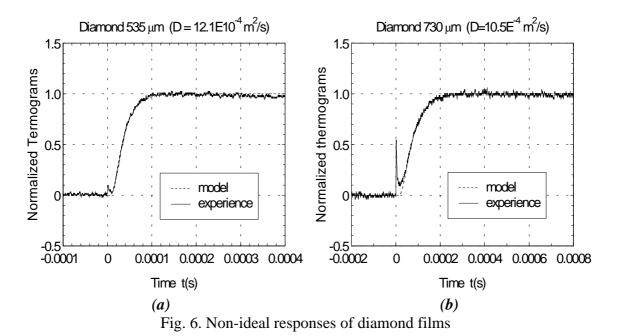


Fig. 5. Flash response of a diamond film

The values obtained for diamond films diffusivities are very important. A factor larger than 8 or 10 compared with usually good conductive materials (Gold-Copper-Silicium) (see. Table I.). They vary with respect to the quality of the films. The values obtained for optical quality films (very clear samples) are very close to the natural diamond diffusivity. As for non-diamond films, one also obtained 2D and semi-transparence effects (see Fig. 6.).



The methods we have implemented for the estimation give quite satisfactory results. Parker's method and ordinary Least Squares's Method are very close and reproductibility tests are good. Estimation of the standard deviations on parameters are less than 5%.

Table I: Experimental Results for Non-diamond and Diamond films

Non-Diamond Films				Diamond films				
Sample #	e (µm)	Diffusivity $D(\text{cm}^2/\text{s})$		Sample #	e (µm)	Diffusivity $D(\text{cm}^2/\text{s})$		
		Parker	$O.L.S^*$			Parker	$O.L.S^*$	
1	630	0,87	0,87	1	525	9,20	9,23	
2	630	0,81	0,81	2	565	12,14	12,19	
10	250	0,77	0,76	3	500	9,90	9,83	
15	250	0,76	0,76	4	730	10,46	10,45	
20	250	0,73	0,73	5	535	9,11	9,26	
25	255	0,76	0,74	6	535	11,80	11,84	
3	565	1,53	1,52	7	505	8,82	8,83	
4	520	1,50	1,51	8	705	10,77	10,57	
5	550	1,52	1,52	Gold		1,	1,27	
6	545	1,52	1,53	Copper		1,16		
7	565	1,53	1,56	Silicium		0,92		

* O.L.S: Odinary Least Squares method = Gauss-Newton's method

5. RADIATIVE TRANSFER

The diffusivities results given above are obtained by estimations based on a purely conductive model. The semi-transparent behavior of the samples can affect the diffusivity measurement technique. One can show that the interaction of radiative and conductive transfer can be reduced in the flash method by the use of reflective coatings, especially for materials whose optical thickness is low (thin film with weak absorption coefficient). In contrast, with emitting coatings, interaction is large and the diffusivity is composed of the phonic diffusivity component (intrinsic thermophysical property) related to the purely conductive transfer and of a radiative component which depends on the optical properties of both coatings and sample and on the sample thickness [8].

It is important to notice that even though the *peak* is less pronounced for an absorbing medium (thick optical thickness), the thermograms can also be affected by radiative transfer. To measure this effect, a more general radiative-conductive coupled model must be implemented. An analytical solution of this model in transient state is given in reference [9].

6. CONCLUSION

The diffusivity of 500 microns thick diamond films in the direction perpendicular to their faces has been measured by a heat pulse technique. Particular attention has been paid to the preparation of the sample, to the quality of the laser beam energy distribution and to the signal that was actually measured. The influence of radiative transfer inside the semi-transparent has been shown.

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